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Early History

Much of science and technology is based squarely upon knowledge gained from the use of X rays over the past 75 years. The Naval Research Laboratory (NRL) has been involved in the exploitation of X rays since the 1920s. In the 1930s, Drs. Robert Mehl and Charles Barrett performed seminal X-ray diffraction measurements on complex metallurgical samples. In the 1940s, Dr. Herbert Friedman and his colleagues began rocket X-ray astronomy, which opened a new field of high-energy astrophysics leading to many notable achievements in the 1950s and beyond. Also in the 1940s, Drs. Jerome Karle and Herbert Hauptman began the work on X-ray diffraction that would produce remarkable results in the 1950s and a Nobel Prize for them in 1985. From that same era, Dr. Isabella Karle pioneered practical methods for X-ray structural analysis.

In the 1950s, LaVerne Birks demonstrated the practical utility of X-ray spectrochemical analysis by using both X-ray fluorescence and electron impact excitation. That work led to a major effort starting in the 1960s on X-ray spectroscopy of plasmas, including measurements on nuclear weapons at a Nevada test site as well as numerous multimillion-degree laboratory plasmas. This plasma research led to the development of sources for X-ray lithography in the 1970s. The 1980s saw NRL scientists exploit the remarkable capabilities of synchrotron radiation to determine the structure and properties of a wide range of materials.

The NRL synchrotron radiation story begins with three sabbaticals. In 1974, the first author spent a year at Oxford University during which time he participated in experiments on both the old

Daresbury synchrotron in the United Kingdom and on the ACO storage ring in Paris, France. The second author was at the National Bureau of Standards (NBS) (presently National Institute of Standards and Technology) in 1978 and worked on the Synchrotron Ultraviolet Radiation Facility. And in 1980, the third author pioneered high-pressure diamond anvil experiments at the Stanford Synchrotron Radiation Laboratory. These sabbaticals laid the groundwork for later synchrotron radiation projects involving numerous NRL scientists. Here we give a brief description of the generation and characteristics of synchrotron radiation and review highlights of current research.

Synchrotron Radiation

When electrons or positrons orbiting within an evacuated torus interact with and are accelerated by the strong magnetic fields that steer them around a curved path, they emit synchrotron radiation [1]. The name resulted from the initial observation of "light" in synchrotron particle accelerators built for high-energy physics experiments. Such radiation was a waste of energy from the particle—quite literally, "scrap photons."

Energy is supplied to orbiting particles by synchronous radio frequency fields (synchrotron action) or by linear or other means of particle acceleration followed by injection into a storage ring. The spectrum, intensity, and direction of synchrotron radiation depend on the particle energy and the strength and configuration of the magnetic fields. Figure 1 indicates this schematically. The particles orbit the storage ring in discrete groups or bunches with an energy

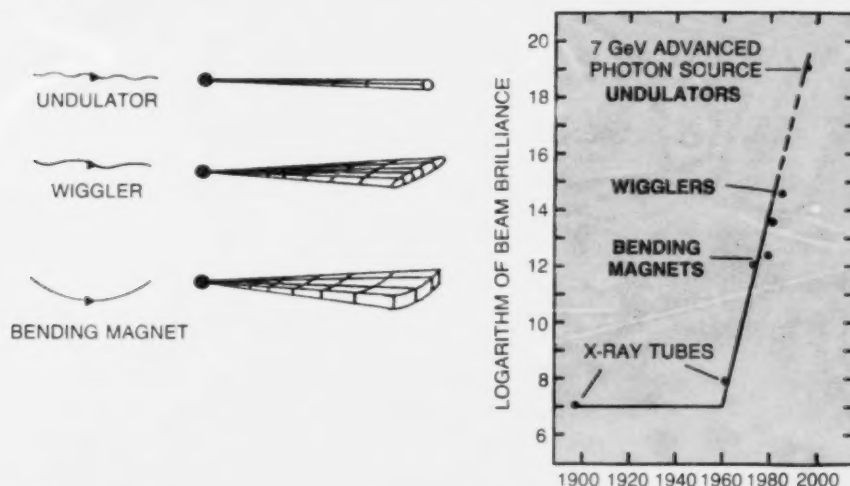


Fig. 1 — At the left-hand side are top views of the paths of electrons through bending magnets, strong alternating-field wigglers, and weaker alternating-field undulators. The X-ray patterns for each case are sketched in perspective. The graph on the right-hand side shows the relative intensities from X-ray tubes and the three types of synchrotron sources. Note that undulators will produce radiation one hundred billion times as brilliant as X-ray tubes.

typically in the range 0.5- to 10-billion electron volts (GeV). The steering (bending) magnets, with fields of about 1 T (10,000 G), cause the particles to emit into a horizontal fan a smooth, continuous spectrum that ranges from the infrared to the hard-X-ray region. The brilliance of bending magnet sources is typically 100,000 times that of the best laboratory X-ray sources. Brilliance is a standard synchrotron radiation unit that takes into account both source size and the angular spread of the beam. It measures the maximum amount of radiation that can be delivered to a small sample.

If a strong, spatially alternating magnetic field produced by a device called a wiggler is employed, the radiation is enhanced by another factor of 10 to 100. If a magnet with more numerous but weaker field oscillations called an undulator is employed, then the X-radiation brilliance can be increased by a factor of as much as 10,000 when compared to a wiggler. Undulator radiation is strongly peaked at certain wavelengths and resembles radiation from free electron lasers.

Most of the early synchrotron radiation experiments in the 1960s and 1970s were done parasitically by using bending magnets on

high-energy machines. They proved so promising for physics, chemistry, biology, and material science that in the 1980s, numerous dedicated synchrotron facilities were constructed at costs of tens of millions of dollars. A number of facilities throughout the world will be completed this decade to satisfy this increasing demand. The three largest ever built—one each in Europe, Japan and the United States—will begin operation around 1995. These facilities will have energies in the 6- to 8-GeV range and consist primarily of undulators and wigglers. Undulators on these storage rings will put up to 100 W/mm² of radiation on a sample. This extraordinary advance in brilliance, illustrated in Fig. 1, goes far to explain the large investments that the U.S. and many other countries have made.

The ten orders of magnitude increase in brilliance from X-ray tubes to synchrotron X-ray sources is reminiscent of the immense difference between lasers and ordinary light sources. Synchrotron radiation is neither stimulated nor strongly coherent. However, the high intensity, small source size, directionality, and short-pulsed character are laserlike. Will synchrotron radiation

have the broad and commercial impact of lasers? The facility size will preclude this. However, the importance of synchrotron radiation for research in a number of fields already rivals that of lasers.

NRL at the National Synchrotron Light Source (NSLS)

Prime among the dedicated synchrotron radiation facilities in the U.S. is the NSLS at Brookhaven National Laboratory on Long Island, New York, shown in Fig. 2. Construction on this \$100M facility began in the late 1970s, and it is currently the world's largest and most productive synchrotron radiation facility with nearly 100 experimental stations in use or under construction.

In the early 1980s, with the support of Dr. Alan Berman, then NRL's Director of Research, NRL and NBS formed one of the first participating research teams (PRTs) at NSLS. Other PRTs at NSLS include organizations such as IBM, AT&T,

Bell Labs, Exxon, several DoE laboratories, and numerous universities. NRL is the only DoD laboratory that formed a PRT. The function of each PRT was to design, construct, and operate one or more beam lines linking the storage ring to experiments.

Beam lines are complex vacuum systems that collect radiation from the storage ring, manipulate it, and focus it onto samples in the experimental stations. They comprise various combinations of valves, apertures, and shutters with precision focusing mirrors, diffracting crystals, gratings or multilayers, and associated safety instrumentation. The experiments are conducted inside bathroom-sized enclosures (called hutches) or within elaborate surface science chambers with many additional sample preparation and diagnostics capabilities. In 1980, NRL began building two beam lines and NBS two more on ports X23 and X24 of the NSLS. Figure 3 shows the end stations of the NRL beam lines.



Fig. 2 — The National Synchrotron Light Source. The annular section of the building houses a 2.5 GeV electron storage ring 170 m in circumference. (Photo courtesy BNL).

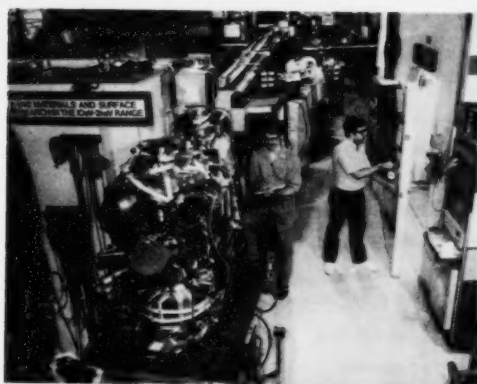


Fig. 3 — NRL beam lines at NSLS. The ultrahigh vacuum surface science chamber for the soft-X-ray line is in the left foreground, and the experiment hutch for the hard-X-ray line is on the right-hand side. Synchrotron radiation reaches the experiments through the vacuum pipes in the background.

To associate a given structural feature or process with a specific species of atom, one generally tunes the synchrotron radiation to excite a transition characteristic of that particular atom. We designed the soft-X-ray beam line to cover a spectral range where there are strong, distinct, core-level transitions in the atoms that make up many of the most important semiconductors, insulators, and metals. Examples are the K edge of carbon; the L edges of silicon, gallium, and arsenic; the K and L edges of nitrogen, oxygen, and aluminum. We also included the valence region in the ultraviolet where transitions occur from the uppermost, filled bands. These provide information concerning the all-important electronic properties but are generally not atom specific.

The soft-X-ray beam line is based on a unique monochromator that was designed and patented by NRL scientists [2]. It uses diffraction gratings, crystals, or multilayers to select a narrow band of synchrotron radiation at a chosen energy in the range from the ultraviolet to several kilovolts. The beam is focused to a size of 1 mm^2 or less at the sample under investigation.

Either of two interchangeable, ultrahigh vacuum experiment chambers terminates this

beam line. One contains a reflectometer, which allows us to measure reflected, scattered, or absorbed X rays. The other chamber, which is evident in the left foreground of Fig. 3, enables us to perform a variety of surface science experiments, particularly photoelectron emission spectroscopy. Ultrahigh vacuum conditions are essential to preserve clean, well characterized surfaces. The beam line and instrumentation were developed to facilitate measurements in three principal areas: X-ray optical properties, surface science, and fast transient phenomena. To initiate the latter, we use a pulsed laser coincident with the synchrotron radiation. This particular array of capabilities is, we believe, unmatched by any other beam line in the world.

The second NRL beam line is for diverse, hard-X-ray experiments in the 4- to 10-keV range [3]. The line is used to measure the absorption, diffraction, and fluorescence of X rays. The main objective of these measurements is to determine atomic structures and environments in complex materials that are important in a wide variety of NRL programs. X-ray spectrochemical analysis of trace elements and calibration of detectors employed in plasma physics have also been performed on this beam line. In contrast to the soft-X-ray line with its two interchangeable end stations, the hard-X-ray line has a fixed hutch. Inside it, various experiments are set up and removed, all controlled remotely from outside the hutch in conformity with radiation safety requirements with hard X rays.

The newest NRL capability at NSLS resides on the superconducting wiggler beam line X17, which provides intensities more than ten times higher than those available from bending magnets. NRL's access to this wiggler line came about through the efforts of the third author, who organized a team for high-pressure research in 1985. This group consists of scientists from 11 institutions, including DoE, private labs, universities, and industry. Use of the wiggler beam line is not limited to solid-state research. It has already been employed to measure the crystal

structure of submicron metallic filaments. Chemical analyses of the metallic elements in wood are planned on the wiggler line.

Research Examples

Here we describe examples of recent research on each of the three beam lines. Much of the work has been carried out in collaboration with other NRL divisions.

Soft-X-Ray Optics: Our work has concentrated on multilayer reflectors in various forms and uses the reflectometer designed for this beam line by Hunter and Rife [4]. This reflectometer allows the incidence and scattering angles to be varied with high precision, and the plane of polarization of the synchrotron radiation is varied by rotating the entire ultrahigh vacuum chamber housing the reflectometer. Very few reflectometers exist in the world that have similar capabilities.

The fundamental problem with X-ray optics is that, as the photon energy increases above ~ 20 eV, mirrors made of homogeneous metals (for example, platinum or gold) cease to reflect efficiently except at extreme grazing angles of incidence. For platinum, the grazing angle must be about 2° or less for appreciable reflectivity at or above 2 keV. But grazing incidence reflecting optics, such as those used in telescopes and in most synchrotron radiation beam lines, are subject to severe aberrations and must be figured to extreme tolerances that are costly to achieve.

An X-ray multilayer increases reflectivity so that near-normal instead of grazing-incidence optics can be used, resulting in substantially improved image definition and larger apertures. It is the X-ray analog of multilayer interference coatings used to increase or decrease the reflectivity of visible optics. Multilayers are designed to give enhanced reflectivity over a specific band of wavelengths.

X-ray multilayers are made by depositing alternating layers of two different materials, repeating the process through 10 to 100 layer

pairs. The multilayers reflect because the two constituent materials are chosen to have different scattering coefficients. Note that visible multilayers use refractive index variation rather than scattering, but since the refractive index of all materials is near unity in the soft-X-ray range, index variation will not work here. Typical material combinations include W-C and Mo-Si. Since the thickness of a layer pair has to be roughly a half wavelength, thickness and smoothness must be controlled at a single atom level. Technology to do this has evolved in the last decade. A good multilayer coating can yield a normal-incidence reflectivity of 20% or more, increasing toward lower grazing angles. Uncertainties in materials parameters, thicknesses, and smoothness demand that the properties of a given multilayer be measured as well as calculated, providing an important diagnostic function for synchrotron radiation.

X-ray multilayers can be applied directly to diffraction gratings, allowing them to be used at angles of incidence considerably larger than those possible for the bare grating. This represents one of the most promising applications for multilayers, and NRL has been a leader in this area. Rife and coworkers measured substantial increases in grating reflectivity, although multilayer deposition techniques must improve before the reflectivities become comparable to those predicted by theory [5]. Figure 4 gives an example of a spectrum reflected from a W-C multilayer on a blazed grating, which in this instance was mounted in the beam-line monochromator. The grating was scanned in a high order (8th) to optimize the match between the grating parameters and the multilayer spacing. An Al filter cuts off the light at the high-energy end, and structures arising from absorption in the photodiode detector (Ga) and beam line optics (Ni) are evident. The multilayer results in a smooth spectrum with substantially higher throughput.

Many of the multilayer measurements are done by or in collaboration with scientists in NRL's Space Science Division and at Lawrence

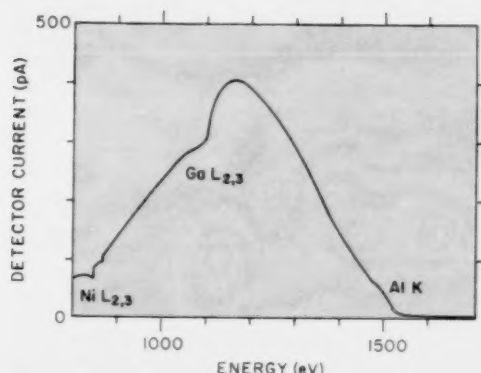


Fig. 4 — Monochromator scan with the W-C multilayer grating and mirror mounted as diffraction elements. The multilayer grating is scanning in 8th order. Measurements made through an Al filter 0.00025-in. thick.

Livermore National Laboratory. Some of this research provided analyses of X-ray optics for an SDI program on nuclear directed energy weapons managed by the Condensed Matter and Radiation Sciences Division.

Semiconductor Surface Passivation:

Photoelectron emission spectroscopy (PES) is a major tool of surface science. In combination with a tunable synchrotron radiation source, PES can be sensitive to surface atoms and molecules at coverages much less than a monolayer. PES can differentiate between processes that occur either primarily in the bulk or at the surface, can distinguish the effects of initial and final electron states, and can provide information about electron momentum as well as energy inside a material. These capabilities are one reason why surface science has become a principal product at synchrotron radiation facilities. Surface science has evolved into one of the most complex and demanding disciplines of material science. Nevertheless, it concerns many of the most important modern technologies and is used effectively by many groups at NRL.

A second, ultrahigh vacuum chamber for the soft-X-ray beam line houses our PES experiments at NSLS. This instrumentation is used to attack a formidable problem of semiconductor device

technology, the passivation of GaAs surfaces. The research was carried out in collaboration with workers from NRL's Electronics Science and Technology Division and from Wake Forest University.

To passivate a semiconductor surface is to reduce the loss of charge carriers through surface recombination. The usual method is to oxidize the surface simply by passing O_2 over it. Bermudez and collaborators [6] found that by using molecular nitric oxide (NO) rather than O_2 , the oxidation could actually be made to proceed faster at 300 K and at relatively high NO exposure. To identify intermediate species in the reaction, they extended their measurements down to temperatures in the 40 to 140-K range and looked carefully at PES in the range that includes the Ga 3d and As 3d core levels and valence excitations of NO. Figure 5 shows spectra for the clean GaAs surface, a thin film of NO on GaAs, and a thick film of NO. The progressive changes evident in the spectra of (d) and (e) illustrate the oxidation of the surface by a photochemical reaction produced by the synchrotron radiation acting over a time span of minutes. The curves show the relative number of photoelectrons that leave the surface with a given energy; the height of a peak is a measure of the quantity of the species that causes the peak. The features to note in (c), (d), and (e) are the drop in the peaks on the right-hand side due to solid NO and the consequent rise of the oxygen-related satellite near the As 3d peak on another oxygen feature around 82 eV. These and similar data gave strong evidence that, at low temperatures, both thermal and photochemical oxidation occur by a $(NO)_2$ dimer dissociating into an adsorbed oxygen atom and N_2O molecule that leaves the surface. It is possible, in effect, to follow this process from physisorption to reaction to dissociation and desorption. However, there are indications that at temperatures above 100 K, where reactions proceed much faster, a species other than N_2O (perhaps NO^+) is the intermediate in the oxidation.

These experiments illustrate that synchrotron radiation is sufficiently intense to allow us to

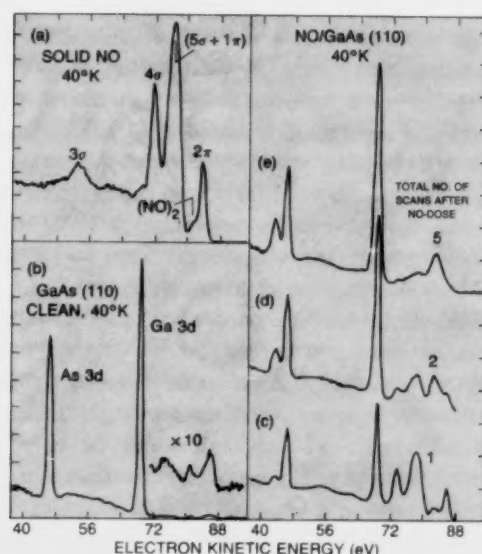


Fig. 5 — Photoemission data at 92 eV photon energy for: (a) solid NO at 40 K; (b) clean GaAs (110); and (c)–(e) a thin NO film after increasing exposure to SR. The labels 3 σ , etc., in (a) refer to various molecular orbitals of NO. The inset in (b) shows an expanded valence band spectrum.

observe and identify small quantities of a molecule on a clean surface in times brief enough (depending on temperatures) to allow identification of transient reactions.

Surface Electron Dynamics: The performance of many electronic devices comprising semiconductors and insulators is often affected by surface states whose electron populations can change in times ranging from seconds to nanoseconds or faster. Important processes, including voltage shifts, loss of current carriers through surface recombination, and photochemical reactions that change the surface can occur as a result of these states. Thus we felt that the rewards for developing time-resolved, synchrotron radiation techniques to identify and characterize these states would be substantial.

Our approach was based on the fact that electrons circulating in a storage ring are grouped in well-separated bunches of duration one nanosecond or less. Synchrotron radiation from one bunch generally is not intense enough to

perturb electronic states measurably. However, a pulsed laser can easily produce measurable perturbations. Thus the two sources were joined to create a repetitive pump–probe experiment, where the pump is a laser pulse and the probe is a burst of synchrotron radiation exciting photoelectrons that can be detected. This required Long and collaborators [7] to develop electronics to synchronize the laser pulse with the synchrotron radiation pulse and to accumulate PES data over nanosecond intervals, not a trivial task. A copper vapor laser has been used so far because its repetition rate is high (6 kHz), its 2.43-eV photon is strongly absorbed in most semiconductors, and its 5-ns pulse is adequately matched to the synchrotron radiation pulse.

To provide background for the experiments, consider how the energy bands of a semiconductor can change as one scans from bulk to surface. If there is no net surface charge, the bands will not change in energy to within an atomic layer or two of the surface. That is, the bands are flat. But if there are surface states in the energy gap between the valence and conduction bands that can trap charge and create a surface potential, the bands will gradually bend, and consequently carrier concentrations will change on approaching the surface. However, if the region near the surface is suddenly flooded with electrons and holes by a laser pulse, the resultant high conductivity will no longer allow the electric field to exist, and the bands will immediately flatten. The excess electrons and holes will begin to decay by several processes, the most interesting being diffusion to and recombination at the surface. The states through which surface recombination occurs can be the same as or different from those that originally trapped the charge that caused band bending. By following the decay of this transient potential or photovoltage in time, one can learn much about transport and recombination processes near the surface. We shall now describe a pioneering combined laser–synchrotron radiation experiment carried out by Long and others that was able to accomplish this [7].

Space-Charge Dynamics on Silicon: The dominance of silicon-based technology dictates that it continue to be one of the most intensely investigated materials, and current research is providing important new information about silicon surfaces. To illustrate results from our laser-synchrotron-radiation research on Si, Fig. 6 shows data for a p-type Si(111) surface saturated with hydrogen. These data were obtained by monitoring the transient shift of the Si 2p core level determined from photoemission. Because of positive charge in surface states, the bands are bent in the dark by about 0.5 eV. During the 5-ns laser pulse, the surface potential changed by an amount ΔV , the photovoltage. Data points in Fig. 6 show the measured decay of ΔV after laser pulses at three different fluences. The fact that reasonable data can be obtained over a range of almost 10^5 in laser fluence indicates the power of the technique.

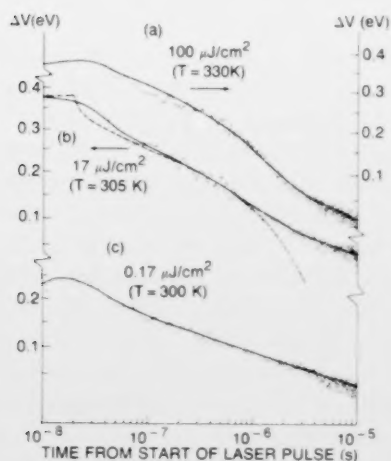


Fig. 6 — Photovoltage (ΔV) decays for a hydrogen saturated, p-type, Si(111) surface for four different laser fluences. Points are experimental data, solid lines are the numerical simulation, and the dashed line is an analytic simulation.

An important parameter characterizing the decay—the so-called surface recombination velocity—was obtained by fitting the experimental

data with a numerical transport code, PISCES IIB, which is often used for device modeling. The solid lines are results from this code, and the agreement with the experiment is impressive. The surface recombination velocity for this particular surface turns out to be relatively high. In quantitative terms, the probability is greater than 10% that any hole striking the surface recombines there. Comparison with the numerical model also reveals a previously unappreciated effect of transient space charge separation caused by the trapping of electrons or holes in the surface-potential well arising from the recovered band bending. Note that the dashed line in Fig. 6, which is a good analytic simulation one might use in lieu of the numerical code but which does not include this charge separation effect, fails to match either the experiment or the numerical result.

One of the most significant points of this work and one that purely electrical measurements (e.g. photocapacitance) cannot address is the observation that, even with the high electron and hole concentrations that the laser can produce near these Si surfaces, the photoemission spectra all shift rigidly by ΔV and return to their initial energies at some time after the pulse. This shows that the underlying electronic structure remains unaffected. Clearly it would be extremely interesting if this were not the case—that is, if bands actually changed shape or new excited bands appeared. Such changes do occur on GaAs, as we next describe.

Photochemistry on GaAs: Since the surface quality of compound semiconductors is generally poorer than for Si and surfaces are less well understood, they represent an important target for combined laser-synchrotron radiation techniques. Initial measurements on clean GaAs surfaces produced anomalous results, and it soon became apparent that a new photochemical phenomenon was taking place. Goldenberg and Long were using very low laser intensities, being careful to avoid excessive heating of the surface. They were thus surprised when photoelectron emission data

showed that the surface was decomposing under laser irradiation [8]. Stable islands of metallic Ga were forming on the surface at intensities so low that the overall temperature rise was 13°C or less. With such a small temperature rise, there is no doubt that the process is photochemical. While new in itself, this phenomenon is related to several other processes of obvious technological significance. For example, laser irradiation can substantially enhance the etch rate of GaAs exposed to a chlorine atmosphere. Low intensity irradiation can also cause large decreases in the efficiency of photoluminescence. At generally higher intensities, changes in surface lattice structure and emission of constituent species have been observed. For several of these experiments, photochemical mechanisms have been suggested but not proved.

Most of our Ga-island experiments do not directly employ time resolution. A clean GaAs surface is irradiated for a short time, after which any changes are measured by means of PES. Looking first at the photoelectron energy distribution in the valence band region, Long and collaborators saw that as laser irradiation proceeded, electron states were building up in the band gap at and below the Fermi level. This suggests that metal is being produced on the surface. In the surface sensitive Ga-3d core spectra, they also noted the growth of a small shoulder on the main band, a known signature of Ga metal. Aside from this shoulder, the Ga-3d (and the As-3d) spectra changed very little in shape and magnitude indicating that most of the surface remains as it was initially, and the metallic Ga is isolated in islands that cover a small fraction of the surface. There is no evidence that the As released with the Ga remains on the surface, and As leaving the surface has been detected.

One reason this process has not been previously described is its relatively low efficiency. One Ga atom is added to an island for roughly 10^7 photons incident from the copper vapor laser. It appears likely that the laser produces electrons and holes that recombine at the

surface, some providing energy to remove a Ga atom that is weakly bound at a surface step or defect and transport it to a Ga island. Needless to say, the individual steps of this photochemical process are of great interest and are being explored, as are broader questions concerning relationships to the performance of various electro-optic devices.

Time-resolved laser-synchrotron radiation experiments contributed to our GaAs work but in a way different from that for the Si research just described. At these GaAs surfaces, the band bending is generally not homogeneous. When photoelectron spectra are measured coincident with the laser pulse, electrons and holes made by the laser effectively smooth out the inhomogeneous potentials, thus sharpening the spectra considerably and making their various components more distinct. In fact, on p-type GaAs, it was necessary to use time resolution to make quantitative measurements of the Ga-island contribution.

The Ga islands are also seen directly by using scanning electron microscopy (Fig. 7). The micrographs show islands that are roughly hemispherical and that have diameters up to several hundred angstroms, depending on exposure. Interestingly, the islands seen in the micrographs are entirely consistent with our more detailed data obtained with synchrotron radiation.

Local Atomic Structure: Extended X-ray absorption fine structure measurements (EXAFS), were virtually unknown before the advent of electron storage rings for synchrotron radiation. However, EXAFS is currently the most frequently used technique on hard-X-ray beam lines. The attenuation of radiation in matter is generally represented by an absorption coefficient $\alpha(E)$, which depends on the photon energy E ; this dependence is especially strong in the vicinity of an absorption edge. Typically a beam of radiation emerging from the storage ring is first diffracted by one or more crystals to select a narrow energy

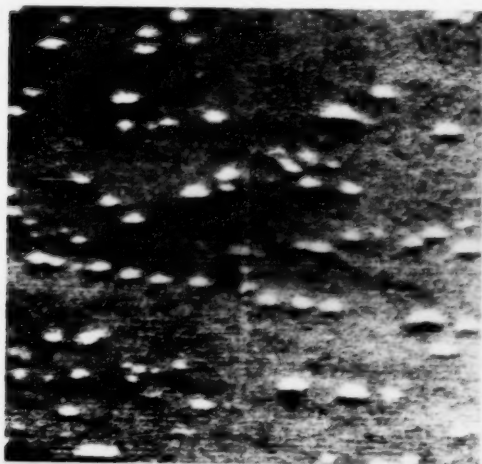


Fig. 7 — Scanning electron micrograph of laser irradiated GaAs(110) surface. Electron beam at 20° grazing incidence. The area shown is 400-nm wide.

band of photons. This filtered beam is then directed onto the sample. By varying the angle that the monochromating crystal(s) makes with the beam, the incident photon energy can be tuned. The monochromatic beam is then directed to the sample and $\alpha(E)$ is measured. As the photon energy passes through an absorption edge of any element in the sample, a significant increase in $\alpha(E)$ is observed due to ionization of that element. For energies above the absorption edge, the $\alpha(E)$ curve exhibits a series of complex undulations; the oscillations from about 50 eV to 1 or 2 keV above the edge are the EXAFS. They result from scattering of the primary photoelectrons by the neighboring atoms. The reflected electron waves interfere with the outgoing photoelectron wave, resulting in the observed modulation of $\alpha(E)$.

The great attraction of EXAFS measurements is that they give information about the number, proximity, and thermal vibrational amplitudes of the atoms neighboring the atom in question. That is, EXAFS is element specific. Thus the absorption spectra of a complex chemical mixture can be readily sorted out in terms of the environment of a particular atom. In this manner, EXAFS provides structural data complementary to that obtained by conventional diffraction. Synchrotron radiation is

required because the beams that are available from conventional X-ray tubes are too weak to permit acquisition of most EXAFS spectra in reasonable time periods and often have a complex energy structure of their own that precludes interpretation of the data.

Three important materials problems were recently solved by EXAFS experiments on beam line X23B. In one case, we are able to explain the abrupt decrease in the rate of change of the ordinary optical index of refraction with increasing Ti dopant in LiNbO_3 . In another, we solved the crystallographic structure of a unique metastable cobalt film. And in the third case, we obtained information relating to the aging properties of activated carbon filter materials for gas masks.

The material most widely used for ferroelectric optical waveguide devices is Ti-diffused LiNbO_3 . Prior to this EXAFS work, there was little understanding of how the Ti is incorporated into the LiNbO_3 lattice and, more importantly, why its presence has such a pronounced effect on the optical index of refraction. Based on careful absorption measurements above the Ti edge on a series of samples with varying Ti concentrations, Skeath, Elam, and collaborators were able to demonstrate that the position of the Ti^{4+} ion is concentration-dependent and tends to become disordered for higher concentrations [9]. The dependence of the optical indices on Ti concentration was then calculated based on this positional information, resulting in a much clearer understanding of the relationship between optical properties and impurity site geometry. This work was done in collaboration with NRL's Optical Sciences Division.

Another important materials problem that was solved with EXAFS data is the crystallographic structure of metastable Co films. Based on total energy calculations, it was concluded that a metastable body-centered cubic phase of Co should be possible, but prior to the work mentioned here, no direct confirmation of its

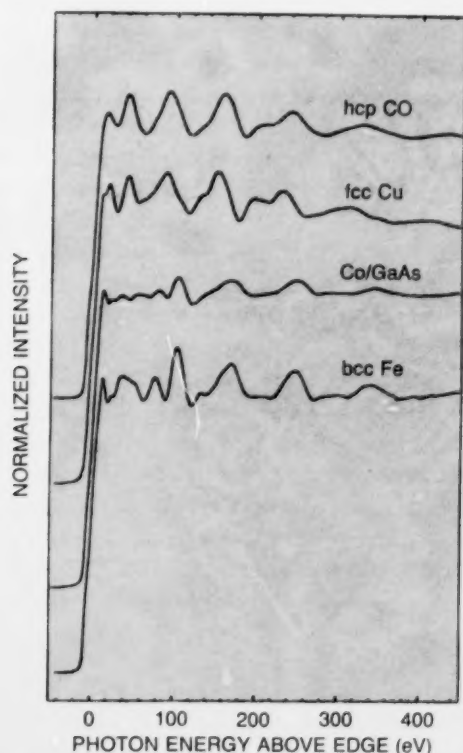


Fig. 8 — EXAFS spectra for HCP-Co, FCC-Cu, Co film deposited on GaAs, and BCC-Fe

existence had been found. One reason was that Co films are grown by molecular-beam-epitaxy techniques on GaAs substrates, and the lattice parameter of the Co very nearly matches half that of the GaAs. Consequently, conventional diffraction studies produce signals from both the Co epilayer and the substrate, and the signal from the Co is lost in that from the GaAs. By carefully measuring the EXAFS above the Co edge, Idzerda, Elam, and collaborators obtained data specifically from the Co film and identified its structure as body-centered cubic with a lattice parameter of 2.88 Å [10]. Figure 8 shows EXAFS spectra obtained from the Co film and three standards for comparison—hexagonal close-packed Co, face-centered cubic Cu, and body-centered cubic Fe. Although detailed information is obtained from Fourier transforms of

these spectra, it is clear that the Co spectrum more nearly resembles that of body-centered cubic Fe than of the other structures. This work, done in collaboration with NRL's Materials Science and Technology Division, provides an excellent example of a case where the element-specific nature of EXAFS experiments is vital.

Our third example, impregnated carbon, is used to remove toxic vapors from air streams. Despite years of study, little is known about the structure of the adsorbents or the chemistry occurring on the carbon. This is especially true for the chemical changes on aging. If this chemistry can be understood, new treatments to improve performance, reduce degradation by aging, and provide alternate compositions can be developed. EXAFS studies designed to address this problem were carried out on behalf of the Army Chemical Research and Development Center and the Naval Surface Weapons Center. EXAFS data recorded from appropriate activated carbon samples were used to determine the oxidation states and site geometries of copper and chromium on the carbon surface. The results show that both of these elements are involved in the chemistry of the aging process [11]. More specifically, by comparing data obtained from unaged and 60-day aged carbon samples, the following conclusions are drawn: The Cr is in a mixed oxidation state, containing both Cr^{+6} and Cr^{+3} . The oxidation state decreases on aging, and the local site geometry changes significantly. For the Cu atoms, the oxidation state is initially Cu^{+2} and does not appear to change as the material ages, although there is some indication of movement by the Cu atoms on aging. Thus both the Cr and the Cu are involved in the aging process, and the chemical changes are irreversible for both elements. On the basis of our work, DoD sponsors are presently engaged in further efforts to improve the performance of these carbon filter materials.

Crystal Structures from X-Ray Diffraction: Structural analysis of biological materials is another major field of synchrotron

radiation research. Protein crystallography, from which one can determine the detailed structure of a constituent molecule, is of particular interest. We cite as an example work on the green fluorescent protein aequorea by Perozzo and Ward of NRL's Laboratory for the Structure of Matter [12]. This protein is interesting because of its fluorescence properties. It is often difficult to grow single crystals of proteins large enough for conventional X-ray analysis; in the case of aequorea, Perozzo and coworkers were able to grow crystals of average dimension <0.5 mm. Figure 9 shows a hexagonal specimen. They used 1.63 Å monochromatic radiation from the NRL hard-X-ray beam line to obtain good X-ray diffraction photographs. These data enabled them to determine the structures of both hexagonal and monoclinic crystals while keeping exposures brief enough to avoid damaging the samples—a significant problem with many biological materials.

The highest static pressures that can be generated in a laboratory (in excess of several million atmospheres) are developed by reducing the area over which the force acts to microscopic dimensions and by applying the force through the hardest known substance, diamond. The diamond-anvil pressure cell has evolved to

become the single most important research tool in high-pressure science. An important feature offered by the diamond-anvil cell is a relatively low absorption coefficient for a broad spectrum of radiation. This advantage is employed to monitor some of physical properties of the sample by measuring transmitted or reflected radiation from the pressure cavity. If X rays are used, the effect of pressure on the structure of samples can be determined. However, the extreme pressures are achieved at the expense of sample volume; typically, a sample pressurized in a diamond-anvil cell occupies a volume of about 10^{-15} m³, or about one picoliter. Thus if conventional X-ray sources are employed, extremely long exposure times—tens or even hundreds of hours—are usually needed to obtain useful structural information. Synchrotron radiation reduces the exposure time from days or weeks to minutes or seconds [13].

For high-pressure structural studies of polycrystalline or powder samples, the method of choice is energy-dispersive diffraction, which uses unfiltered synchrotron radiation. The diffracted X rays are analyzed at a fixed angle with an energy-sensitive detector. Diffraction peaks occur at those photon energies that satisfy the Bragg condition for the various crystallographic

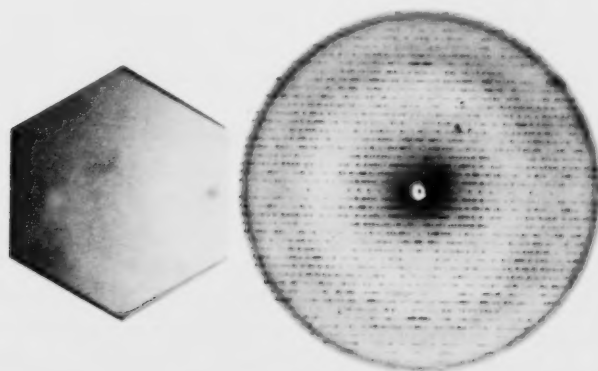


Fig. 9 — Micrograph of half-millimeter crystal of aequorea green fluorescent protein and diffraction of pattern recorded at NSLS by NRL's Ms. Mary Ann Perozzo and Dr. Keith Ward, and Drs. Richard Thompson and William Ward, of the Rutgers University

planes in the sample. From the positions of the peaks, one obtains information about the interatomic spacing and symmetry of the sample. These data are then interpreted in terms of compressibilities and crystal structures, or phases.

A striking example of our data from the diamond-anvil cell is reproduced in Fig. 10, which shows spectra recorded from a mixed sample of KI and NaCl as the pressure is incrementally increased from 0.83 to 3.17 GPa. The lowest energy peak at about 22 keV arises from the (200) planes of KI in the B1, or rocksalt phase; the highest energy peak above 26 keV is the same reflection from the NaCl. The peak at about 25 keV is the (110) peak from KI in the B2, or CsCl phase. At about 1.8 GPa, the KI enters a two-phase region; the (200) peak from its B1 phase and the (110) peak from its B2 phase are simultaneously present. The shift of the NaCl peak is used in combination with the measured temperature and the equation of state of NaCl to calculate the pressure.

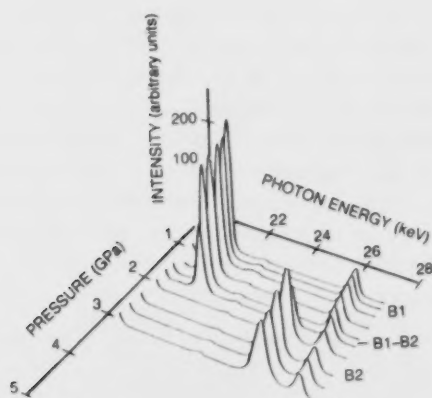


Fig. 10 — Energy dispersive diffraction spectra of the B1-to-B2 phase transition in KI

If a conventional X-ray source were used for this experiment, it would take almost two weeks to collect the data. Instead, each of the 10 spectra shown in Fig. 10 was measured in 2 min. At 1.8 GPa, the KI is in a metastable state, and by monitoring the intensities of the B1 and B2 peaks,

it is possible to determine quantitatively the dynamics of the phase transition. This information is then used to test theories describing the transition mechanism.

Small Samples: The high-pressure experiment described is an example of using synchrotron radiation to analyze small quantities of material. We have used the wiggler beam line to investigate the structure of another type of small sample—ultrafine wires. These were made by NRL's Materials Science and Technology Division by drawing fine glass fibers containing single or multiple metallic filaments [14]. Filaments as small as a few μm can be drawn. By cascading this process and by using glasses with properly selected melting temperatures, it is possible to produce a single-filament wire of sub- μm dimension. Because of the minute sample volumes involved, efforts to obtain structural information by using conventional X-ray sources were unsuccessful. Our recent measurements on a Bi filament 0.22 μm in diameter show it to be a single crystal in its normal, tetragonal structure. Even with the incident X-ray beam collimated to a square 10 μm on a side, there is still ample signal from the sample. By adjusting the position of the sample relative to the incident beam, a variety of single-crystal diffraction peaks are measured. Because the diffraction peaks are measured in the energy dispersive mode as in the high-pressure experiments described, an entire family of reflections can be measured simultaneously. The experiment is far from being signal limited; for example, Fig. 11 shows that the (0,h,2h) peaks can be detected in a measurement period as short as 10 ms. The volume of crystal being illuminated for this measurement is $3.8 \times 10^{-19} \text{ m}^3$, or equivalently, 0.38 femtoliters; this corresponds to a mass of 3.7 picograms, which we believe to be a record minimum sample.

These data further show that the Bi crystal is under a negative linear strain of about 1.4% normal to the fiber axis. The implication is that the crystal is under a hoop stress from the surrounding

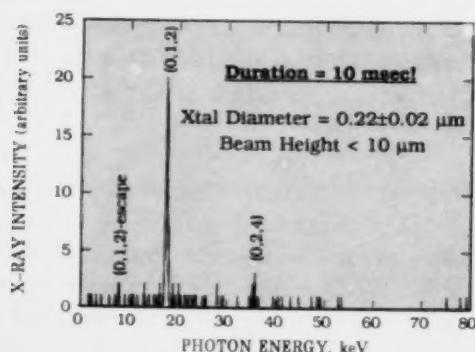


Fig. 11 — Energy dispersive diffraction spectrum of reflections from a $0.22 \pm 0.02\text{-}\mu\text{m}$ diameter bismuth filament

glass sheath. This level of strain corresponds to a residual stress of about 1.7 GPa. It is suspected that this stress results from differential thermal contraction upon cooling. Bismuth is known to undergo a first-order phase transformation from Bi-I to Bi-II at 2.25 GPa. Current efforts are directed toward thinner samples where the residual stress may be sufficient to initiate this phase change. Other research with the wiggler beam line involves very thin films, the objective again being to obtain structural information from a sample that would not be "visible" were conventional X-ray sources employed.

Emerging Research Opportunities

Many studies of the structure and dynamics of surfaces and bulk materials along the lines described continue at NSLS. In addition, NRL scientists continue to develop new lines of research in this time frame, two of which we discuss next.

Much of the X-ray work described is performed without attention to the chemical changes that are induced by the absorption of X rays. Such chemical changes are important in fields ranging from X-ray lithography, in which polymeric molecules are either scissioned or cross linked, to radiation biology, specifically the scission of DNA molecules. The extreme intensity available from the wiggler beam line makes it possible to perform X-ray photochemistry

experiments in reasonable times. For example, Fig. 12 shows a solid plastic that was produced by allowing a beam from the wiggler line to pass through a liquid polymer. The ensuing cross linking increased the molecular weight and produced the solid, which was photographed after decanting the unaffected liquid. Continuing research is expected to be of both scientific and technical relevance. Specifically, X-radiation curing of epoxies may be used for field repair of composites, for example, on aircraft.

Most of the work that uses synchrotron X radiation is aimed at determining the structure of materials, as earlier described. However, X-ray fluorescence induced by synchrotron radiation yields quantitative information on the elemental composition of materials to levels of parts per million. This high chemical sensitivity, combined with the very small, high-intensity beams available from the storage ring, make possible spatially resolved chemical analyses on a wide variety of samples. NRL recently pioneered the application of X-ray fluorescence analysis employing synchrotron radiation to the quantification of metallic elements in wood. For the first time, the fine beam permitted multiple measurements within a single, annual growth ring of the wood samples [15]. Figure 13 shows the distribution with time of several elements in samples of wood. This work is being extended to the quantitative assessment of lead uptake by trees, which is expected to correlate with the amount of lead put

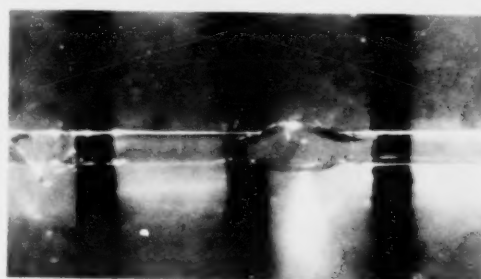
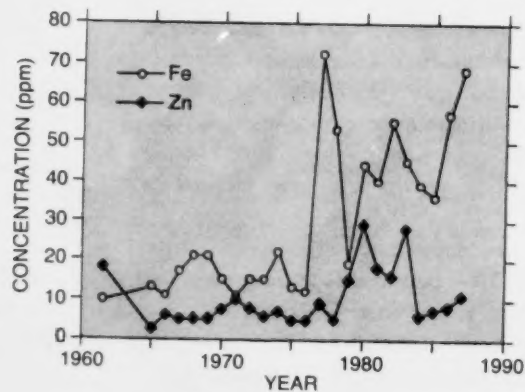


Fig. 12 — Clear polymer filament cured by X-ray beam from X17C wiggler beam line. Filament lays on a scale; dark lines are separated by 1.0 mm.

Fig. 13 — Variation of Fe and Zn over the life of a red oak



into the environment from leaded gasoline. Core samples obtained from the bottom of the ocean or from ice fields can be analyzed in much the same way as the tree rings. Numerous environmental studies are planned involving such retrospective monitoring with synchrotron radiation.

Looking Ahead

NRL scientists plan to continue to work at the leading edge of synchrotron X-ray research. Toward this goal, plans are being made to use the \$500M Advanced Photon Source X-ray Facility now under construction by the Department of Energy at the Argonne National Laboratory in northern Illinois. Figure 14 shows the storage ring, with a circumference of 1.1 km. The linear accelerator and booster synchrotron are located

within the main ring, with laboratory and office spaces around the periphery. Similar facilities are now under construction in France and Japan.

Positrons of 8-GeV energy will orbit in the Advanced Photon Source storage ring, passing through bending magnets, wigglers, and undulators to produce intense, nanosecond bursts of hard X rays with wavelengths suitable for measuring atomic, molecular, and condensed-matter structures. The extreme X-ray intensity, high enough to melt metals in a few seconds, will permit measurements of unprecedented precision. Structural and chemical analyses of materials can be performed down to μm spatial scales. Investigation of phase transformations, chemical changes, and other atomic motions will be possible with a temporal resolution of 100 ps. The high intensity also permits precision monochromators



Fig. 14 — The Advanced Photon Source X-ray Facility under construction by DoE at the Argonne National Laboratory. (Photo courtesy of ANL).

to cut narrow slices out of the synchrotron radiation spectrum to produce energy resolution approaching 10 meV. Similarly, the narrow collimation will permit the measurement of very small angular deflections produced by scattering from samples to resolve very small momentum transfers.

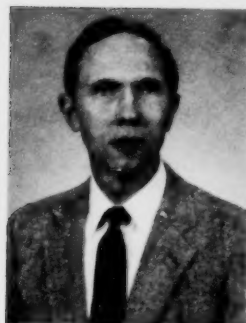
These new capabilities will derive from the unprecedented X-ray brilliance and represent one or more orders of magnitude improvement in the precision of X-ray experiments. The impact of an order of magnitude increase can be appreciated by considering that airplanes fly, on the average, approximately ten times faster than average driving speeds, which are, in turn, approximately ten times higher than walking speeds. For a given travel time, the difference translates into a global reach when compared to a state or country-wide travel or compared to movement around a town or neighborhood. As the NSLS and other synchrotron radiation sources have already done, the Advanced Photon Source will have a strong impact on many areas of science and technology. It will become operational around 1995, the centennial of the discovery of X rays.

References

1. E. E. Kock, ed., *Handbook on Synchrotron Radiation Vol. 1* (North-Holland, Elsevier Science Publishing Company, Inc., New York, 1983).
2. W. R. Hunter, R. T. Williams, J. C. Rife, J. P. Kirkland and M. N. Kabler, "A Grating/Crystal Monochromator for the Spectral Range 5 eV to 5 keV," *Nucl. Instr. and Meth.* **195**, 141 (1982).
3. J. P. Kirkland, D. J. Nagel, and P. L. Cowan, "The Naval Research Laboratory Materials Analysis Beam Line at the National Synchrotron Light Source," *Nucl. Instr. and Meth.* **208**, 49 (1983).
4. W. R. Hunter and J. C. Rife, "An Ultrahigh Vacuum Reflectometer/Goniometer for Use with Synchrotron Radiation," *Nucl. Instr. and Meth.* **A246**, 465 (1986).
5. J. C. Rife, T. W. Barbee, Jr., W. R. Hunter, and R. G. Cruddace, "Performance of a Tungsten/Carbon Multilayer-Coated, Blazed Grating from 150 to 1700 eV," *Physica Scripta* **41**, 418 (1990).
6. V. M. Bermudez, R. T. Williams, G. P. Williams, Jr., M. W. Rowe, H. Liu, A. Wu, H. R. Sadeghi, and J. C. Rife, "Photoemission Study of the Adsorption of Nitric Oxide on Gallium Arsenide (110) at Low Temperature," *J. Vac. Sci. Technol.* **A8**, 1878 (1990).
7. J. P. Long, H. R. Sadeghi, J. C. Rife, and M. N. Kabler, "Surface Space-Charge Dynamics and Surface Recombination on Silicon (111) Surfaces Measured with Combined Laser and Synchrotron Radiation," *Phys. Rev. Lett.* **64**, 1158 (1990).
8. S. S. Goldenberg, J. P. Long, and M. N. Kabler, "Photoemission Study of Low-Fluence, Non-Thermal Laser Damage of UHV-Cleaved Gallium Arsenide (110)," *Materials Research Society Symposium Proceedings*, to be published.
9. P. Skeath, W. T. Elam, W. K. Burns, F. A. Stevie, and T. H. Briggs, "Concentration Dependence of the Octahedral Ti^{4+} Center in $LiNbO_3$: Its Effect on Refractive Indices," *Phys. Rev. Lett.* **59**, 1950 (1987).
10. Y. U. Idzerda, W. T. Elam, B. T. Jonker, and G. A. Prinz, "Structure Determination of Metastable Cobalt Films," *Phys. Rev. Lett.* **62**, 2480-2483 (1989).
11. W. T. Elam and E. F. Skelton, "Report on the Test Plan for Synchrotron Radiation Study of Activated Carbon Surface Chemistry," *NRL Report 9302*, Feb. 1991.
12. M. A. Perozzo, K. B. Ward, R. B. Thompson, and W. W. Ward, "X-Ray

- Diffraction and Time-Resolved Fluorescence Analyses of Aequorea Green Fluorescent Protein Crystals," *J. Biol. Chem.* **263**, 7713 (1988).
13. E. F. Skelton, "Microdiffraction with Synchrotron Beams," *Adv. in X-Ray Anal.* **31**, 1-7 (1988).
 14. J. D. Ayers, "Glass Fibers with Metallic Cores," *1989-1990 NRL Review*, June 1990, pp. 94-97.
 15. J. F. Gilfrich, N. L. Gilfrich, E. F. Skelton, J. P. Kirkland, S. B. Qadri, and D. J. Nagel, "X-Ray Fluorescence Analysis of Tree Rings," *X-Ray Spectrometry*, to be published.

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EARL F. SKELTON received a B.S. degree in physics from Fairleigh Dickinson University in Teaneck, New Jersey, in 1962. He received a Ph.D. degree in physics from Rensselaer Polytechnic Institute in Troy, New York, in 1967 and came to NRL that year as a National Research Council Post-Doctoral Associate. Dr. Skelton has been teaching continuously on a part-time basis since 1968, first at Prince George's Community College, then in the graduate school of the University of Maryland, and at The George Washington University since 1974. He served as a liaison scientist at the Office of Naval Research in Tokyo, Japan, in 1978 and spent a sabbatical year at the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford University in 1980-81. He was elected a Fellow of the American Physical Society in 1980 and served on the Users Organization Executive Committees at both SSRL and the National Synchrotron Light Source (NSLS). He is currently head of the Phase Transformation Section in the Dynamics of Solids Branch and is spokesperson for the Insertion Device Team responsible for Beamline X17C at NSLS. He has authored or co-authored over 200 technical publications, including an encyclopedia article, and has won two NRL publication awards. On a personal note, Dr. Skelton has completed over forty 26.2-mile marathons, including every Marine Corps Marathon.

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